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# GENERAL EXPRESSIONS FOR ACID-BASE TITRATIONS OF ARBITRARY MIXTURES

by

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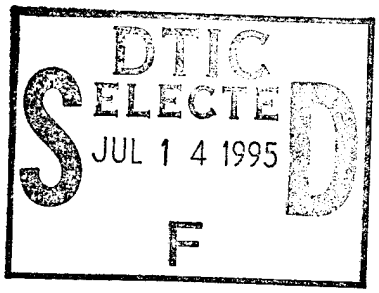


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# GENERAL EXPRESSIONS FOR ACID-BASE TITRATIONS OF ARBITRARY MIXTURES

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**Abstract:** A single, general master equation is given for acid-base titrations, describing the entire progress of the titration, and equally valid for the titration of a single strong acid with a single strong base as for that of the titration of an arbitrary mixture of acids with an arbitrary mixture of bases, or vice versa.

**Introduction.** Acid-base titrations are the backbone of classical quantitative analysis. Initially, color indicators were used to detect their equivalence points, and a rigorous theory for their complete course was neither required nor testable. The advent of pH meters changed that, but the theory did not catch up. Instead, titration curves continued to be described in terms of a number of isolated points (for the onset of the titration, and for each equivalence point) together with approximate intermediate segments not quite connecting those discrete points. While this yields a fairly close approximation for the titration of single, monoprotic acids and bases, it fails for more complicated systems, such as polyprotic acids or bases and their salts, and especially for mixtures of these.

Consequently, for the determination of equilibrium constants from titration curves, special numerical algorithms were developed to fit experimental data. Alternatively, expressions for the various chemical equilibria can be solved by computer as a set of simultaneous equations. While both methods lead to correct results, they are rather non-transparent to the general user.

Earlier we showed that simple, closed-form solutions describing the progress of a titration can be obtained when the traditional approach of writing the pH (the intensive property) as an explicit function of the volume of titrant used (the extensive property) is abolished in favor of the reverse process[1]. This inversion leads to an explicit expression for the titrant volume as a function of pH. Merely by interchanging the axes, the resulting progress curve can be plotted as a titration curve.

In the present communication we will generalize our earlier approach, and extend it to arbitrary mixtures of acids titrated with arbitrary mixtures of bases, or vice versa. This generalization only requires a slight redefinition of the concepts of proton association and dissociation functions.

We begin our derivation with the simple titration of a single acid with a single base, then gradually extend our approach in order to arrive at the final, quite general results. In all cases we start from the charge balance equation. For the sake of conciseness, the supporting algebra will only be shown explicitly for the first example.

**Titrating a single strong monoprotic acid HA with a single strong monoprotic base MOH.** During a titration, we add a volume $V_b$ of base to the fixed acid sample volume $V_a$, so that the total volume $V_a + V_b$ changes continually. We take this into account by writing

$$[A^-] = \frac{C_a V_a}{V_a + V_b} \tag{1}$$

$$[M^+] = \frac{C_b V_b}{V_a + V_b} \tag{2}$$

where $C_a$ and $C_b$ refer to the *initial* total analytical concentrations of acid and base respectively, and are therefore constant during the titration, while $[A^-]$, $[M^+]$, $[H^+]$ and $[OH^-]$ change. The terms $V_a/(V_a+V_b)$ and $V_b/(V_a+V_b)$ describe the mutual dilution of the sample by the titrant, and vice versa.

We now introduce the charge balance

$$[H^+] + [M^+] = [A^-] + [OH^-] \tag{3}$$

Upon substitution of eqns.(1) and (2) this becomes

$$[H^+] + \frac{C_b V_b}{V_a + V_b} = \frac{C_a V_a}{V_a + V_b} + [OH^-] \tag{4}$$

which can be rearranged to

$$\{ C_b + [H^+] - [OH^-] \} V_b = \{ C_a - [H^+] + [OH^-] \} V_a \tag{5}$$

From this we calculate the **progress curve** as

$$\frac{V_b}{V_a} = \frac{C_a - [H^+] + [OH^-]}{C_b + [H^+] - [OH^-]} = \frac{C_a - \Delta}{C_b + \Delta} \tag{6}$$

where we have introduced the abbreviation

$$\Delta = [H^+] - [OH^-] \tag{7}$$

For any value of $[H^+]$ we can find the corresponding value of $\Delta$ using eqn.(7), assuming that the ionization product of water is given, and then obtain the value of $V_b/V_a$ from eqn.(6). Therefore, eqn.(6) describes the progress of the entire titration curve. While it is calculated in terms of $V_b$ as a function of $[H^+]$, we can plot it as a traditional **titration curve** of pH vs. $V_b$ if so desired.

**Titrating a single weak monoprotic acid HA with a single strong monoprotic base MOH.** The approach is identical to that just taken, except that the mass balance for the weak acid must include the undissociated acid, i.e., eqn.(1) must be replaced by

$$[HA] + [A^-] = \frac{C_a V_a}{V_a + V_b} \tag{8}$$

We now introduce the concentration fraction

$$\alpha_{A^-} = \frac{[A^-]}{[HA]+[A^-]} = \frac{K_a}{[H^+]+K_a} \tag{9}$$

where $K_a$ is the dissociation constant of the weak acid. Combining eqns.(8) and (9) yields

$$[A^-] = \{[HA]+[A^-]\}\ \alpha_{A^-} = \frac{C_a V_a \alpha_{A^-}}{V_a + V_b} \tag{10}$$

which can be combined with eqns.(2) and (3) to yield

$$\frac{V_b}{V_a} = \frac{C_a \alpha_{A^-} - \Delta}{C_b + \Delta} \tag{11}$$

**Titrating a single polyprotic acid $H_nA$ with a single strong monoprotic base MOH.** In order to extend the above approach to a polyprotic acid we simply replace $\alpha_{A^-}$ by the proton dissociation function $F_a$, which is the weighted sum of the concentration fractions $\alpha$, each weighted by the number of protons lost. It therefore represents the fraction of dissociable protons for the particular species considered, here $H_nA$. The subscript a reflects the Bronsted notion of the acid as a proton donor. Deleting all valencies for the sake of notational simplicity, we have

$$F_a = \alpha_{H_{n-1}A} + 2\,\alpha_{H_{n-2}A} + 3\,\alpha_{H_{n-3}A} + \ldots + n\,\alpha_A \tag{12}$$

where

$$\alpha_{H_mA} = \frac{[H]^m K_1 K_2 \ldots K_{n-m}}{[H]^n + [H]^{n-1} K_1 + [H]^{n-2} K_1 K_2 + \ldots + K_1 K_2 \ldots K_n} \tag{13}$$

with $m = 1, 2, \ldots, n$, while

$$K_m = \frac{[H]\,[H_{n-m}A]}{[H_{n-m+1}A]} \tag{14}$$

This leads to the expression

$$\frac{V_b}{V_a} = \frac{F_a C_a - \Delta}{C_b + \Delta} \tag{15}$$

**Titrating acid salts.** The above result can be extended to an acid salt by appropriately defining the proton dissociation function $F_a$ . For example, for phtalic acid, here denoted as $H_2A$, eqn.(12) leads to

$$F_a = \alpha_{HA^-} + 2\,\alpha_{A^{2-}} \tag{16}$$

while we can define $F_a$ for potassium hydrogen phtalate, KHA, as

$$F_a = \alpha_{A^{2-}} - \alpha_{H_2A} \tag{17}$$

where the weighting factor 1 indicates the loss of one proton in going from $HA^-$ to $A^{2-}$, and the factor -1 the gain of one proton (formally, the loss of -1 protons) in going from $HA^-$ to $H_2A$.

**Titrating an arbitrary mixture of acids with a single strong monoprotic base.** Because the charge balance equation (3) is strictly additive in the weighted concentrations of the various ionic species present (weighted by their respected valencies), we merely have to modify eqn.(15) for a mixture of acids to

$$\frac{V_b}{V_a} = \frac{\Sigma\, F_a\, C_a - \Delta}{C_b + \Delta} \tag{18}$$

**Titrating a weak monoprotic base B with a strong monoprotic acid HA.** Here the roles of sample and titrant are reversed, and we find

$$\frac{V_a}{V_b} = \frac{C_b\,\alpha_{HB^+} + \Delta}{C_a - \Delta} \tag{19}$$

where

$$\alpha_{HB^+} = \frac{[HB^+]}{[HB^+]+[B]} = \frac{[OH^-]}{[OH^-]+K_b} = \frac{[H^+]}{[H^+]+K_a} \tag{20}$$

and

$$K_a\,K_b = K_w = [H^+]\,[OH^-] \tag{21}$$

**Titrating a polyprotic base with a strong monoprotic acid.** By analogy with eqns.(12) and (15) we find

$$\frac{V_a}{V_b} = \frac{F_b\,C_b + \Delta}{C_a - \Delta} \tag{22}$$

where the proton association function

$$F_b = \alpha_{HB} + 2\,\alpha_{H_2B} + 3\,\alpha_{H_3B} + \ldots + n\,\alpha_{H_nB} \tag{23}$$

accounts for the fraction of dissociable protons that can be bound to the particular species (here: a polyprotic base), again deleting the valencies. The subscript b denotes the role of a base as a proton acceptor.

**Titrating an arbitrary mixture of acids with an arbitrary cocktail of bases.** This generalization follows directly as

$$\frac{V_b}{V_a} = \frac{\Sigma F_a C_a - \Delta}{\Sigma F_b C_b + \Delta} \tag{24}$$

**Titrating an arbitrary set of bases with any number of acids.** To complete the general discussion, we now reverse the roles of acid and base. This can be done either by derivation ab ovo, or simply by inversion of eqn.(24) to

$$\frac{V_a}{V_b} = \frac{\Sigma F_b C_b + \Delta}{\Sigma F_a C_a - \Delta} \tag{25}$$

**A single expression for the progress curve.** A fully protonated acid can only lose protons, and $F_a$ is obviously an appropriate function to use. Likewise, for a fully deprotonated base, $F_b$ would be our first choice. For an acid salt, matters are more ambiguous, because it can in principle be titrated as an acid or as a base; it can therefore be described in terms of either possible proton loss or possible proton gain. Fortunately there is no real problem here, because we always find that $F_a = -F_b$ . We can therefore extend the use of $F_b$ to all species involved in acid-base equilibria. By defining $F = -F_a = F_b$ for each species participating in the titration we can then condense eqns.(24) and (25) into a single general relation in terms of *t*itrant and *s*ample properties,

$$\frac{V_t}{V_s} = - \frac{\Sigma F_s C_s + \Delta}{\Sigma F_t C_t + \Delta} \tag{26}$$

**The function F.** Functions similar to F, $F_a$ and $F_b$ are widely used in the literature, often denoted[2,3] by symbols such as Z or n. There is, however, a subtle difference with these earlier symbols, because they were usually not tied to the particular species used in the sample and titrant but, instead, to the entire acid-base system considered. This makes them notationally less convenient to use when the sample is a mixture. The same applies to the use of the degree of completion of the titration, $\phi$ .

Below we will illustrate the use of F by considering orthophosphoric acid and its sodium and ammonium salts. For $H_3PO_4$ we have

$$F = F_b = - F_a = - \alpha_{H_2PO_4^-} - 2\,\alpha_{HPO_4^{2-}} - 3\,\alpha_{PO_4^{3-}} \tag{27}$$

For the monosodium salt $NaH_2PO_4$ we have

$$F = F_b = - F_a = - \alpha_{HPO_4^{2-}} - 2\,\alpha_{PO_4^{3-}} + \alpha_{H_3PO_4} \tag{28}$$

and for $NH_4H_2PO_4$

$$F = F_b = -F_a = -\alpha_{HPO_4^{2-}} - 2\,\alpha_{PO_4^{3-}} + \alpha_{H_3PO_4} + \alpha_{NH_3} \quad (29)$$

Likewise we find for $Na_2HPO_4$

$$F = F_b = -F_a = -\alpha_{PO_4^{3-}} + 2\,\alpha_{H_3PO_4} + \alpha_{H_2PO_4^-} \quad (30)$$

and for $(NH_4)_2HPO_4$

$$F = F_b = -F_a = -\alpha_{PO_4^{3-}} + 2\,\alpha_{H_3PO_4} + \alpha_{H_2PO_4^-} + 2\,\alpha_{NH_3} \quad (31)$$

Finally, for $Na_3PO_4$ we have

$$F = F_b = -F_a = \alpha_{HPO_4^{2-}} + 2\,\alpha_{H_2PO_4^-} + 3\,\alpha_{H_3PO_4} \quad (32)$$

and for $(NH_4)_3PO_4$

$$F = F_b = -F_a = \alpha_{HPO_4^{2-}} + 2\,\alpha_{H_2PO_4^-} + 3\,\alpha_{H_3PO_4} + 3\,\alpha_{NH_3} \quad (33)$$

For mixtures, each component of a mixture contributes its own F and its own concentration C to the appropriate summation in eqn.(26), where F and C pertain to the original composition of sample or titrant. Equations (24) through (26) can be used at any pH in, e.g., a 'universal' buffer mixture.

**Discussion.** The most immediate usefulness of eqns.(24)-(26) lies the fact that they can readily be applied to any acid-base titration, given the initial composition of sample and titrant. They apply to the titration of acids, bases, their salts, and arbitrary mixtures of the above, and they allow direct comparison with experimental data. No sophisticated computer programs are needed. Of course, the simple formalism hides the mathematical complexity associated with polyprotic acids and bases, because the specific equilibrium constants enter only in the calculations of the various concentration fractions $\alpha$ which define the F's. However, since these $\alpha$'s can always be expressed directly in terms of $[H^+]$ and the appropriate equilibrium constants, the entire calculation is straightforward and non-iterative, the type of computation which can be done, e.g., on a spreadsheet. The availability of a general yet exact solutions also makes it easier to verify the validity of approximations used in, e.g., Gran plots[4] and Schwartz plots[5], to determine the precise locations of equivalence points for complicated samples.

Since the reasoning used is based solely on the validity of the charge balance equation, which itself derives from the electroneutrality requirement for macroscopic volumes, the formalism is completely general. Activity corrections will of course affect the various equilibrium constants, and will thereby make the functions F weakly dependent on the ionic strength (unless the latter is kept constant) and on any other factors affecting activity coefficients. When activity corrections are needed, iterations become unavoidable, but the calculations can still be made readily, even on a spreadsheet[6], since the uncertainties inherent in ionic activity coefficients seldom justify more than a single iteration.

The dilution correction used in eqns.(1), (2) and (8) does not take into account any additional dilution from periodic rinsing of the inside of the titration vessel. Such additional dilution, non-inherent in the titration, can of course be taken into account, at some additional complexity, but only when the volumes of rinse solution used and the pH at which they were added are known. This unnecessary complication is therefore best avoided when quantitative data are desired.

Equations (24) through (26) indicate at precisely what level the titration curve of a mixture of acids or bases is additive in the components of that mixture, something a numerical simulation cannot do. It also provides an interesting link with the proton condition often used in equilibrium pH calculations. For example, at the onset of a titration, before any titrant has been added, $V_t$ in eqn.(26) must be zero, so that the same must also apply to $\Sigma F_s C_s + \Delta$ . Inspection of $\Sigma F_s C_s + \Delta = 0$ shows that it is, indeed, the proton condition for the sample, written in standard form, i.e., with all its parameters on the left-hand side. Likewise, $\Sigma F_t C_t + \Delta = 0$ is the proton condition for the titrant. Similar considerations apply to eqns.(24) and (25).

The quantities $\Sigma F_s C_s + \Delta$ and $\Sigma F_t C_t + \Delta$ appearing on the right-hand side of eqn. (26) implicitly depend on $[H^+]$, both through $\Delta$ and, for weak acids and bases, through the functions F. At the beginning of the titration, $V_t$ is zero, and so is $\Sigma F_s C_s + \Delta$ , which one can use to compute the pH of the sample. When the titration is continued far beyond its equivalence point(s), $V_t/V_s$ will tend to infinity, and $\Sigma F_t C_t + \Delta$ will approach zero; from $\Sigma F_t C_t + \Delta = 0$ we can find the pH of the titrant. During the progress of the titration, $[H^+]$ assumes values intermediate between these two extremes, making neither $\Sigma F_s C_s + \Delta$ nor $\Sigma F_t C_t + \Delta$ zero; in this range, $V_t/V_s$ will assumes finite, positive values.

The model presented here extends our earlier formalism[1] in a way that is more conducive to treating mixtures. A similar approach can be applied to redox titrations[7], in which case we have

$$\frac{V_t}{V_s} = - \frac{\Sigma F_s C_s}{\Sigma F_t C_t} \qquad (34)$$

where F now accounts for electrons gained rather than protons. (The absence of a term equivalent to $\Delta$ stems from the fact that, for good reasons, the oxidation and reduction of the solvent are neglected in such models.) This extension makes it possible to calculate the redox titration curves of arbitrary mixtures of oxidizable or reducible species, provided that such curves can be described in terms of equilibrium parameters.

Finally we use three examples to illustrate the usefulness of the present approach. The first merely shows how some analytical problems can be answered much more directly when one calculates the titrant volume $V_t$ as a function of pH rather than the other way around. Likewise, the second and third examples illustrate the rather minimal effort needed for the calculation of the titration curves of rather complex mixtures when using the approach presented here.

**Example 1: the titration error.** The estimation of the titration error is a typical analytical problem. For example, given the acid-base equilibrium constants, one may want to estimate the likely error associated with the range over which an indicator changes its color. The pH limits of the color range have been tabulated, and one merely needs to calculate the corresponding titrant volumes. We note that this corresponds to our approach, in that specific pH values (here: the extremes of the pH range of the indicator) are given, and the corresponding titrant volumes must be computed. Therefore the calculation is straightforward: one selects the pH extremes of the indicator range, calculates $V_t/V_s$ for these limits, and determines the resulting titration error as the difference between this and the equivalence point value of $V_t/V_s$. Similarly, for a potentiometric titration, the titration error resulting from any presumed or anticipated reading error $\Delta$pH can be obtained immediately.

For our illustration we calculate the titration error associated with the use of different color indicators in the titration of 10 mM acetic acid with 10 mM NaOH, using the transition ranges listed by Bányai[8]. Taking the $pK_a$ of acetic acid as 4.76, we calculate the pH at the equivalence point as 8.23, and therefore select as possible indicators cresol red (with a pH transition range given[8] as 7.2 to 8.8), $\alpha$-naphtolphthalein (listed range 7.3 to 8.7), cresol purple (range 7.4 to 9.0), thymol blue (range 8.0 to 9.6), and phenolphthalein (range 8.2 to 10.0). Consequently we merely calculate $V_b/V_a$ for the corresponding values of $[H^+]$. For example, for pH = 7.2 we have $[H^+] = 6.31 \times 10^{-8}$ M so that equation (9) yields $\alpha_{A^-} = 0.9964$ and $V_b/V_a$ is obtained from eqn. (11) as 0.9964 . For pH = 8.8 we likewise find $V_b/V_a = 1.0012$ , so that the pH transition range of cresol red leads to a range of values of from -0.36% to +0.12% around the equivalence point value $V_b/V_a = C_b/C_a = 1.0000$. Table 1 lists the corresponding error ranges similarly calculated for the above indicators; the computation is so simple that it can easily be performed for a number of indicators, even on a pocket calculator, thereby enabling the analyst to make a rational, optimal choice of available indicators. In the present example, cresol red, $\alpha$-naphtolphthalein or cresol purple would make satisfactory indicators, while use of phenolphthalein would not be recommended.

Table 1

This conclusion is, of course, no better than the numerical data on which it is based. Insofar as the pH transition ranges are estimates for usually undefined ionic strengths, and the $pK_a$ is a value extrapolated to infinite dilution, conclusions from theoretical computations are always subject to experimental verification. However, the point of the present example is to illustrate that the present approach makes it quite easy to obtain numerical estimates of the likely titration errors, starting from measured data, whatever their inherent limitations. The method is no different for the titration of a mixture, except that one should then use eqn.(26) instead of eqn.(11).

**Example 2: a universal buffer for use with metal cations.** A 'universal' buffer mixture contains acids chosen such that, over a considerable pH range, the pH is an approximately linear function of the volume of base added. The $pK_a$-values of the components of universal buffer mixtures often lie quite close together, a situation that causes great difficulties in the traditional, mathematical description of the resulting titration curves. The formalism given here does not suffer from such complications, and is well-suited for such calculations, which can readily be performed on, e.g., a simple spreadsheet.

Many proposed universal buffer mixtures contain anions known to form complexes with a variety of metal cations, and are therefore of rather limited usefulness for inorganic studies. Bips et al.[9] described a series of buffers based on 2,6-dimethylpyridines that show very limited affinity for many commonly used cations, including $Li^+$, $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Zn^{2+}$, $Cu^{2+}$ and $Ni^{2+}$. Here we will illustrate the ease of calculating the resulting titration curve by considering two such buffer mixtures. The first one is composed of an equimolar mixture of three components: 3-nitro-2,6-dimethylpyridine ($pK_a$ = 2.87), 2,6-dimethylpyridine-3-sulfonic acid ($pK_a$ = 4.80), and 2,6-dimethylpyridine ($pK_a$ = 6.96).

In this case, we can use equation (18) where, for each component, $F_a$ is simply given by eqn. (9) as $F_a = \alpha_{A^-} = K_a/([H^+]+K_a)$ ; the individual $K_a$-values follow immediately from the listed $pK_a$ values. The resulting curve for the titration with 0.3 M NaOH of a mixture containing all three components at concentrations of 0.1 M is then described by eqn.(18) with

$$\Sigma F_a C_a = \frac{0.1 \times 10^{-2.87}}{[H^+] + 10^{-2.87}} + \frac{0.1 \times 10^{-4.80}}{[H^+] + 10^{-4.80}} + \frac{0.1 \times 10^{-6.96}}{[H^+] + 10^{-6.96}} \qquad (35)$$

The resulting titration curve is shown in Fig. 1.

Fig 1

When a more nearly linear titration curve is desired, two components with intermediate $pK_a$-values can be included in the mixture. Moreover, the range can be extended somewhat by incorporating yet another component. The resulting mixture might then contain, in addition to the three components already mentioned, 4-cyano-2,6-dimethylpyridine ($pK_a$ = 3.68), 3-acetyl-2,4,6-trimethylpyridine ($pK_a$ = 5.91) and 4-methoxy-2,6-dimethylpyridine ($pK_a$ = 8.04). Again, the calculation of the corresponding progress curve is straightforward. By slightly adjusting the concentrations of the various components (while still, in this example, keeping the total concentration constant at 0.3 M) we can then make the pH a linear function of $V_b$ in the range $3.4 \leq pH \leq 8.1$ to much better than ±0.01 pH, as shown in Fig. 2. Again, the ease of calculating the titration curve of the mixture makes it practical to fine-tune the concentrations of the various sample components in order to make a nearly linear titration curve.

Fig 2

**Example 3: titration of a diprotic acid with a mixture of bases.** The above examples only involved monoprotic acid-base equilibria, but our approach is equally direct when polyprotic acids and bases are used. In that case one merely uses, for any polyprotic acid or base, instead of $\alpha_A$- the appropriate forms of equations (12) and (13) for $F_a$ . Moreover, even though one will seldom choose a mixture as titrant, it can happen anyway. As our last example we therefore indicate how to describe the titration of sulfuric acid with sodium hydroxide contaminated with a relatively small amount of carbonate.

For sulfuric acid we use[11] $pK_{a1} \ll 0$ and $pK_{a2} = 1.99$ . In the calculation, we can select any sufficiently large value for $K_a$ , such as $10^{10}$, so that

$$F_a = \frac{[H^+]K_{a1} + 2K_{a1}K_{a2}}{[H^+]^2+[H^+]K_{a1}+K_{a1}K_{a2}} = \frac{10^{10}[H^+] + 2x10^{10}x10^{-1.99}}{[H^+]^2 + 10^{10}[H^+] + 10^{10}x10^{-1.99}} \qquad (36)$$

We can avoid the inelegant use of such an arbitrary value for $K_{a1}$ as follows. Given that $[H^+]$ and $K_{a2}$ are of the order of 1 or less, while $K_{a1}$ is much larger than 1, we rewrite eqn.(36) as

$$F_a = \frac{[H^+]K_{a1} + 2K_{a1}K_{a2}}{[H^+]^2+[H^+]K_{a1}+K_{a1}K_{a2}} = \frac{[H^+] + 2K_{a2}}{[H^+]^2/K_{a1}+[H^+]+K_{a2}}$$

$$\approx \frac{[H^+] + 2K_{a2}}{[H^+] + K_{a2}} = 1 + \frac{K_{a2}}{[H^+] + K_{a2}} = 1 + \frac{10^{-1.99}}{[H^+] + 10^{-1.99}} \qquad (37)$$

which is the expected result for a strong monoprotic acid plus a weak monoprotic acid.

For sodium carbonate, with[11] $pK_{a1} = 6.35$ and $pK_{a2} = 10.33$, we have

$$F_b = \frac{2[H^+]^2 + [H^+]K_{a1}}{[H^+]^2+[H^+]K_{a1}+K_{a1}K_{a2}} = \frac{2[H^+]^2 + 10^{-6.35}\quad [H^+]}{[H^+]^2 + 10^{-6.35}[H^+] + 10^{-6.35}x10^{-10.33}} \qquad (38)$$

Finally, using the value $K_w = 10^{-14.00}$ for the ion product of water, we obtain the complete expression for the progress of the titration of 0.1 M $H_2SO_4$ with a mixture of 0.09 M NaOH + 0.005 M $Na_2CO_3$ as

$$\frac{V_b}{V_a} = \frac{0.1\left\{1 + \frac{10^{-1.99}}{[H^+] + 10^{-1.99}}\right\} - \left\{[H^+] - \frac{10^{-14.00}}{[H^+]}\right\}}{0.09 + \frac{0.005\left\{2[H^+]^2 + 10^{-6.35}[H^+]\right\}}{[H^+]^2 + 10^{-6.35}[H^+] + 10^{-6.35}x10^{-10.33}} + \left\{[H^+] - \frac{10^{-14.00}}{[H^+]}\right\}} \qquad (39)$$

as shown in Fig. 3, and its inverse (for titrating the base mixture with the acid) in Fig. 4. By now it will be obvious to the reader that, even without invoking the (equally straightforward) example of, say, a hexaprotic acid such as EDTA, the conversion of a relation of the type of eqn.(36) in order to express $[H^+]$ as an explicit function of $V_b$ is usually a hopeless undertaking, whereas the direct calculation of $V_b$ based on an equation such as (36) is direct and uncomplicated.

Figs 3 & 4

The explicit representation of complicated chemical systems unavoidably leads to complicated equations, a direct consequence of the many equilibria that must be taken into account. Nonetheless, the general structure of the explicit expression for the progress curve remains simple: it is, at worst, the ratio of two sums of ratios. It is gratifying that a single master equation can represent all acid-base titrations, including arbitrary acid and base mixtures, in their entirety, and that it is simple enough to be amenable to direct, non-iterative evaluation on a spreadsheet.

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## Legends to figures

Fig. 1. The titration with 0.3 M aqueous NaOH of an aqueous solution containing 0.1 M 3-nitro-2,6-dimethylpyridine ($pK_a$ = 2.87) + 0.1 M 2,6-dimethylpyridine-3-sulfonic acid ($pK_a$ = 4.80) + 0.1 M 2,6-dimethylpyridine ($pK_a$ = 6.96), calculated as explained in the text.

Fig. 2. The titration curve calculated for the titration with 0.3 M aqueous NaOH of an aqueous solution containing 0.034 M 3-nitro-2,6-dimethylpyridine ($pK_a$ = 2.87) + 0.051 M 4-cyano-2,6-dimethylpyridine ($pK_a$ = 3.68) + 0.053 M 2,6-dimethyl-pyridine-3-sulfonic acid ($pK_a$ = 4.80) + 0.051 M 3-acetyl-2,4,6-trimethylpyridine ($pK_a$ = 5.91) + 0.048 M 2,6-dimethylpyridine ($pK_a$ = 6.96) + 0.063 M 4-methoxy-2,6-dimethylpyridine ($pK_a$ = 8.04). Inset: the derivative $d(pH) / d(V_b/V_a)$ versus $V_b/V_a$ , calculated using a moving 5-point quadratic[11], showing that this derivative is constant to within ±1.5% for $0.15 \leq V_b/V_a \leq 0.85$.

Fig. 3. The titration curve, calculated from eqn.(36), for the titration of 0.1 M $H_2SO_4$ with a solution containing 0.09 M NaOH + 0.005 M $Na_2CO_3$ .

Fig. 4. The titration curve for the reverse titration, i.e., of a sample containing 0.09 M NaOH + 0.005 M $Na_2CO_3$ with 0.1 M $H_2SO_4$ , simply calculated as $V_a/V_b = 1/(V_b/V_a)$ where $V_b/V_a$ is given by eqn.(36).

## Table

| indicator | pH range | $V_b/V_a$ range |
|---|---|---|
| cresol red | 7.2 - 8.8 | -0.36 % - +0.12 % |
| α-naphtolnaphthalein | 7.3 - 8.7 | -0.28 % - +0.09 % |
| cresol purple | 7.4 - 9.0 | -0.22 % - +0.19 % |
| thymol blue | 8.0 - 9.6 | -0.04 % - +0.80 % |
| phenolphthalein | 8.2 - 10.0 | -0.00 % - +2.02 % |

Table 1. Estimates of the range in $V_b/V_a$ corresponding to the listed transition ranges[9] of the color indicators shown, for the titration of 10 mM acetic acid ($pK_a$ = 4.76) with 10 mM NaOH at 25°C ($pK_w$ = 14.00).

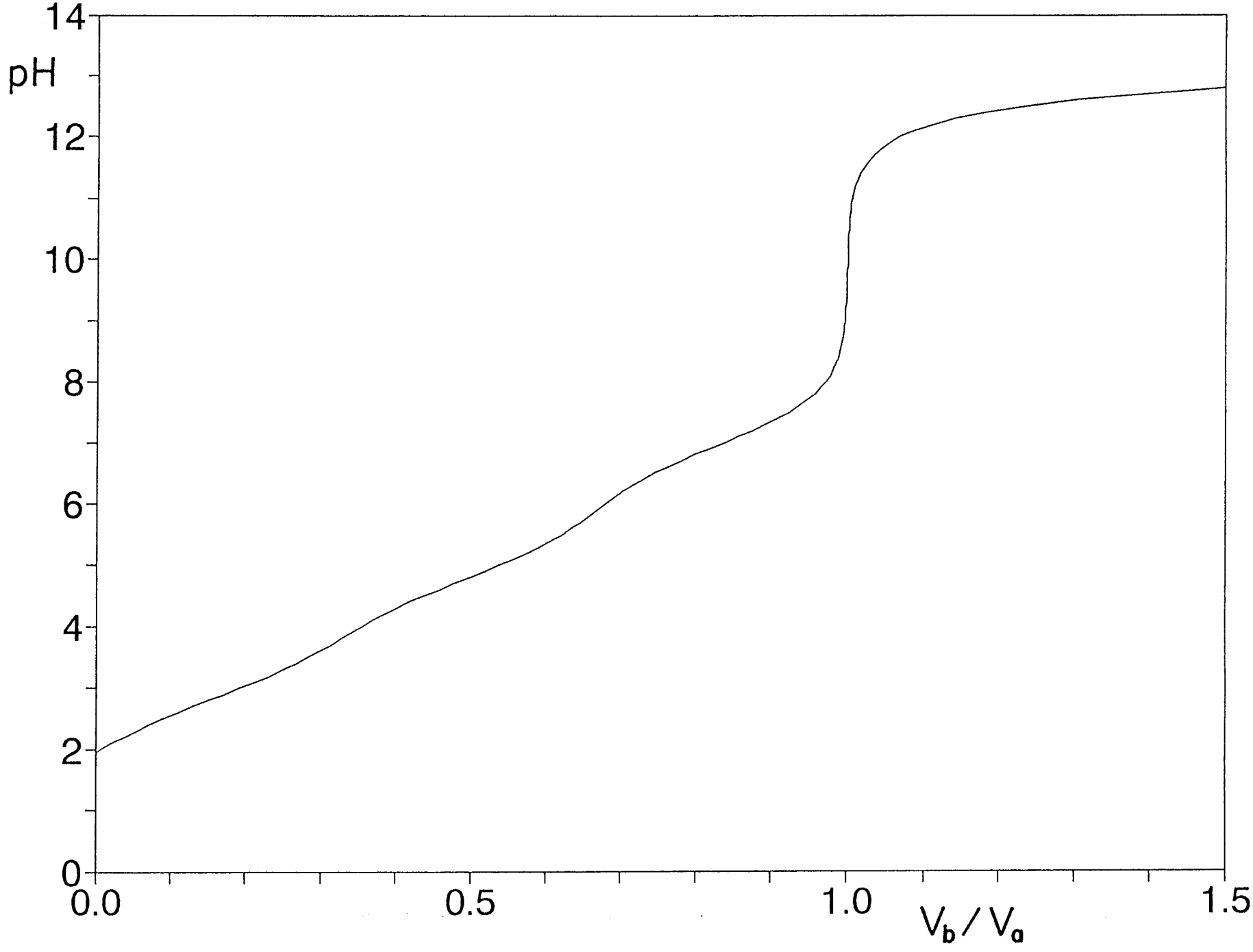


FIG. 1

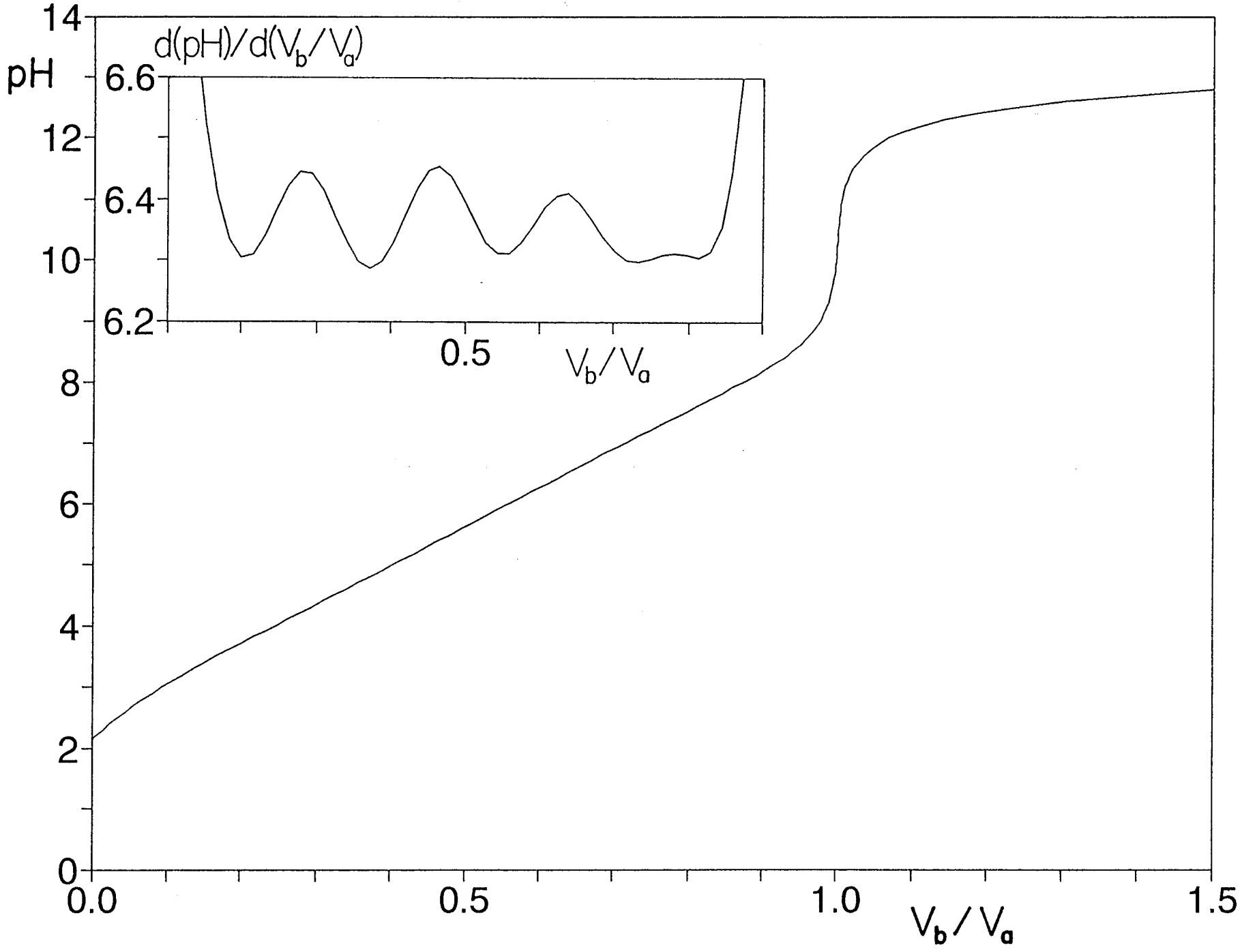


FIG. 2

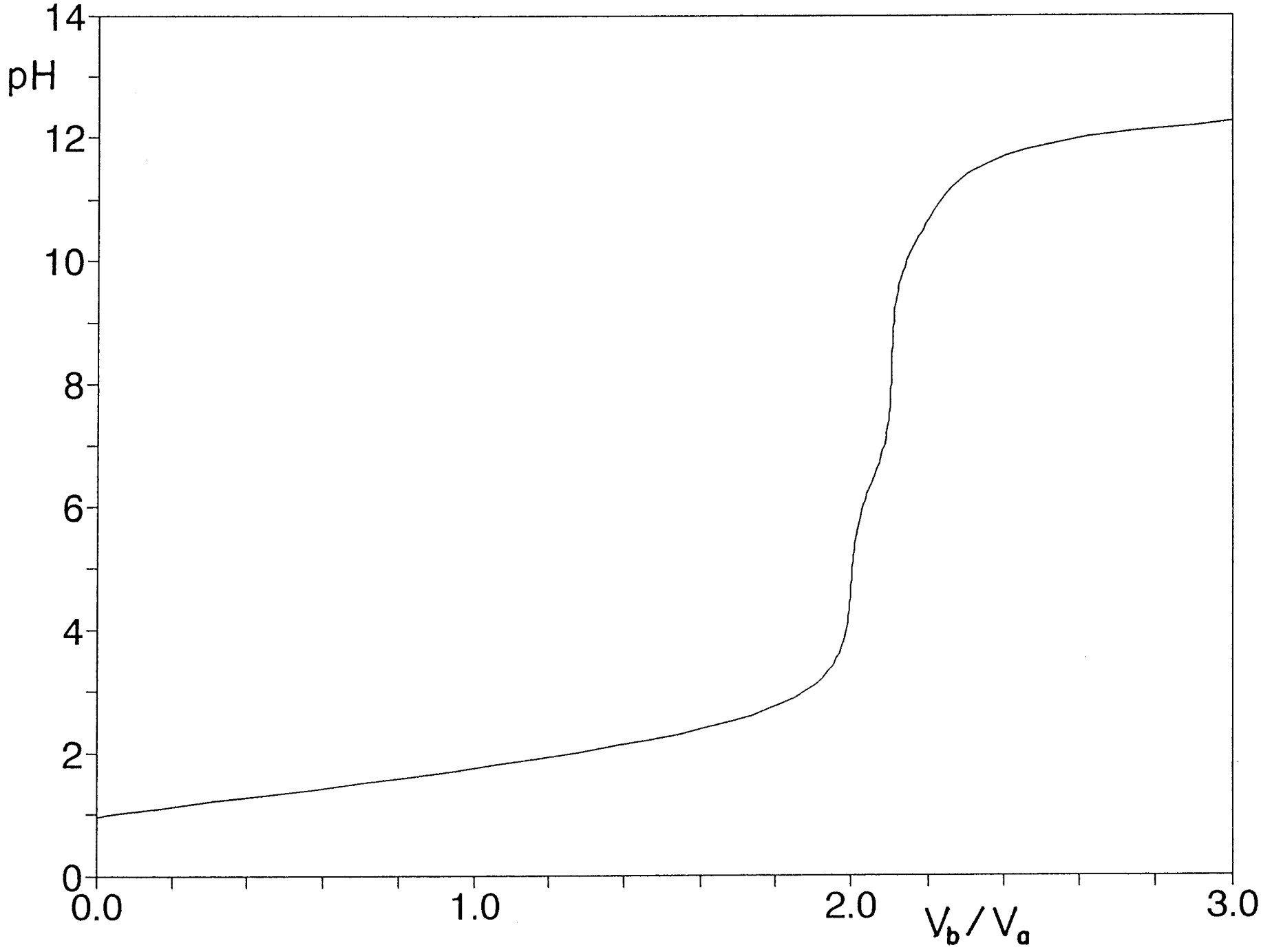


FIG. 3

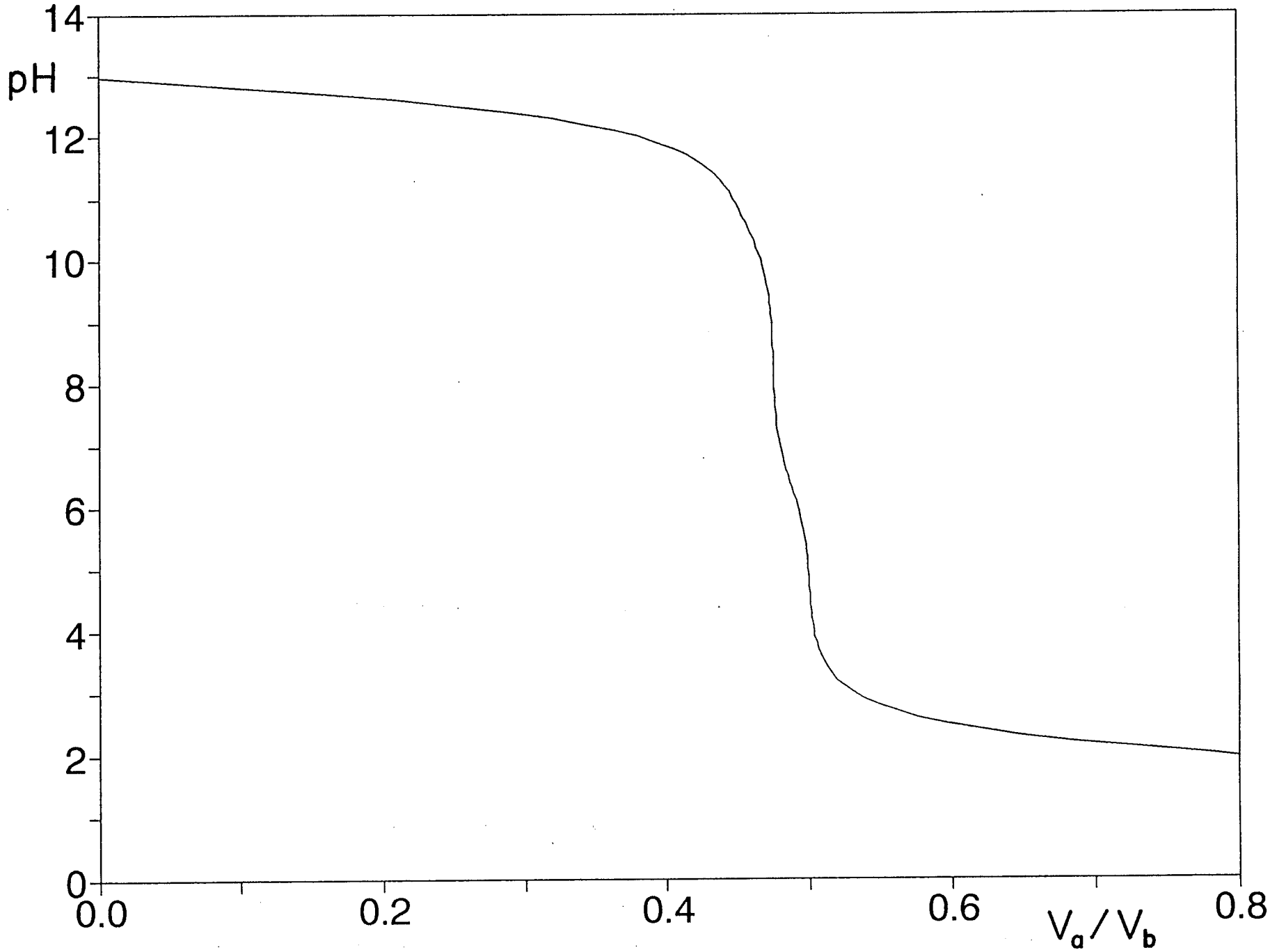


FIG. 4